

# Protocol for isotope dilution using inductively coupled plasma-mass spectrometry(ICP-MS) for the determination of inorganic elements

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**Abstract.** The Comité Consultatif pour la Quantité de Matière(CCQM) endeavours to identify and carry out key activities with the objective of facilitating world-wide comparability and traceability of chemical measurements. Towards this goal, the CCQM has identified comparisons to be carried out using candidate primary methods of chemical analysis. One such method is isotope dilution mass spectrometry. In the first comparison carried out by the CCQM (Study I), the concentrations of various inorganic elements were determined in water solutions using IDMS. The results did not meet the target level of 1% maximum relative deviation from the reference values of the unknowns. It was concluded that more guidance was necessary on the execution of the IDMS method and that a detailed protocol should be developed. Participants would use inductively coupled plasma (ICP) as the ionization source. Here we present the protocol developed for use by CCQM participants in the next comparison (Study III) on the determination of the concentration of lead in water using the IDMS method with an inductively coupled plasma-mass spectrometer.

## 1. Introduction

The measurement needs of trading partners are served when comparability between individual countries and regional alliances is achieved. Measurement comparability between countries and across regions, over long periods of time, is achievable through systems of measurement designed to link to a hierarchy of standards and methods whose results are traceable to the primary SI units and are continuously validated through regular comparisons. Within a region, traceability of measurement results is assured through primary methods and standards at the national metrology standards laboratory level, and the dissemination of transfer standards and methods throughout the region.

From the VIM definition, traceability necessarily involves periodic comparisons to ensure that results agree within stated uncertainties. Regular comparisons are, therefore, needed to establish equivalence of measurements. The Comité Consultatif pour la Quantité de Matière (CCQM) has entered into a process leading to the identification and prioritization of key international comparisons. It has also drafted a description of the characteristics of a primary method and identified candidate primary methods that

appear to fulfill these characteristics. At the CCQM meeting in February, 1996, the committee proposed that "traceability to the SI in measurements of amount of substance or any other quantity requires that the measurements be made using a primary method correctly applied and with evaluated uncertainties" [1].

Primary methods should be tested by simple, straightforward challenges to prove the ultimate attainable level of agreement. Such comparisons, designated "Stage I", are proof-of-principle exercises to test primary methods and develop measurement protocols laying out details of the highest metrological practice for each method. The test samples for these first comparisons should be simple mixtures at concentrations which are relatively easy to measure. The ultimate goal is to achieve the best possible accuracy and precision using the primary method without incurring complications due to the matrix or the blank. Further comparisons can be designed to test the robustness of a primary method when challenged by analyte levels near detection limits and by interference caused by real chemical matrices.

Even before the CCQM was formally constituted, the CIPM Working Group on Chemical Metrology identified Isotope Dilution Mass Spectrometry (IDMS) as a candidate primary method and began a comparison using IDMS to determine the concentrations of a number of inorganic elements in water: the committee designated this Study I. Study I was undertaken by

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laboratories having widely varying experience of the IDOS method. While a few laboratories obtained results in excellent agreement with the reference values for the gravimetrically prepared unknowns, some participants reported results differing by several percent from the reference values. This exercise was valuable because it underscored the importance of developing a robust protocol for each primary method of measurement: only by the rigorous application of such protocols can these methods realize their full potential for accuracy and precision.

In this article we describe a protocol that was written based on our experience at the National Institute of Standards and Technology (NIST) with the high-accuracy determination of heavy metals using IDMS and based on responses from the participants in Study I. We present it separately from the results obtained subsequent to Study I, taking the view that the development of protocols of sufficient rigour to satisfy emerging requirements for measurements of quantity of material is a task of sufficient importance that it should be reported in its own right. Such protocols should not be seen simply as one aspect of a particular comparison.

Here we describe a protocol developed for IDMS determinations using inductively coupled plasma (ICP) as an ionization source. Some of the national metrology laboratories with the most experience in using IDMS for chemical analysis and relative atomic mass measurement, employ thermal ionization mass spectrometry (TIMS) for their most exacting work. ICP-MS, however, is now being used throughout the world and has the potential to make a larger impact on the state of inorganic analysis. The present protocol was designed for use in the third CCQM interlaboratory study, Study III, so it makes specific reference to the determination of lead concentrations in water. To improve on the results obtained in Study I this protocol addresses areas of ambiguity, both conceptual and experimental, which were apparent in that Study. The protocol is designed specifically for ICP-MS, but the basic steps of sample preparation apply equally to TIMS.

It should be noted that some steps in the protocol may not be absolutely required for the determination of lead in water at concentrations of several micrograms per gram. The intention, however, is to show in detail the steps required to obtain results with an accuracy and precision of less than one percent relative, even in samples which are more dilute or are incorporated in a more complex matrix. To emphasize the close relationship between the present article and the protocol it describes, the principal instructions given in the protocol have been left largely in their original form.

## 2. Isotope dilution mass spectrometry

IDMS is based on the addition of a known amount of an enriched isotope (contained in a material called the

“spike”) to a sample. After equilibration of the spike isotopes with the natural isotopes in the sample, mass spectrometry is used to measure the altered isotopic ratio ( $s$ ). The concentration is directly derived from this ratio. A major advantage of the technique is that chemical separations, if required for accurate ratio measurement, need not be quantitative. In addition, ratios can be measured very reproducibly and, thus, concentrations can be determined very precisely.

The IDMS process is outlined in Figure 1. It can be seen from this figure that the technique is based directly on primary standards and the processes of weighing and mass spectrometric isotope ratio measurement. Thus, the weighing process ties the technique to the fundamental SI unit, the kilogram. The mass spectrometric isotope ratio measurement process ties the technique to the relative atomic masses of the elements, linking mass to amount of a substance and thus to the mole, the fundamental unit of chemistry.

The direct link between amount of an element in an unknown sample and a primary chemical standard is also illustrated in Figure 1\*. The accurately known chemical purity of the primary assay standard (B3) is used to obtain an accurate value of concentration for the spike solution (B2) by isotope ratio measurement of a mixture of these two solutions. This procedure is called “spike calibration” (B16), and the process of quantitatively diluting the highly-enriched  $^{206}\text{Pb}$  atom fraction in the spike solution with the isotopically natural assay standard (B11) is often referred to as “reverse isotope dilution.” The spike calibration is an important and integral part of the isotope dilution process, making the analysis a “double ratio” process through the spike to the primary assay standard. That is, isotope dilution analysis requires accurate measurement of the isotope ratios of two mixtures, spike: unknown, and spike: assay standard. If the conditions of ratio measurement are consistent between the spike calibration and the sample measurement, and assuming accurate weighing, potential systematic errors in the measurement process are cancelled or minimized in the final result.

## 3. IDMS measurement of lead in an unknown solution

This section describes the determination, in an IDMS experiment, of the concentration of lead in a solution sample as prepared at the NIST. Because the Pb isotopic composition varies in nature, the isotopic compositions of Pb in the unknown solution and in the assay standard cannot be assumed. This factor necessitates some additional steps in the measurement protocol that would not be needed for most other elements. for

\* Specific boxes in this figure identifying either materials or operations are referred to by the appropriate box label in parenthesis, e. g. (B1).

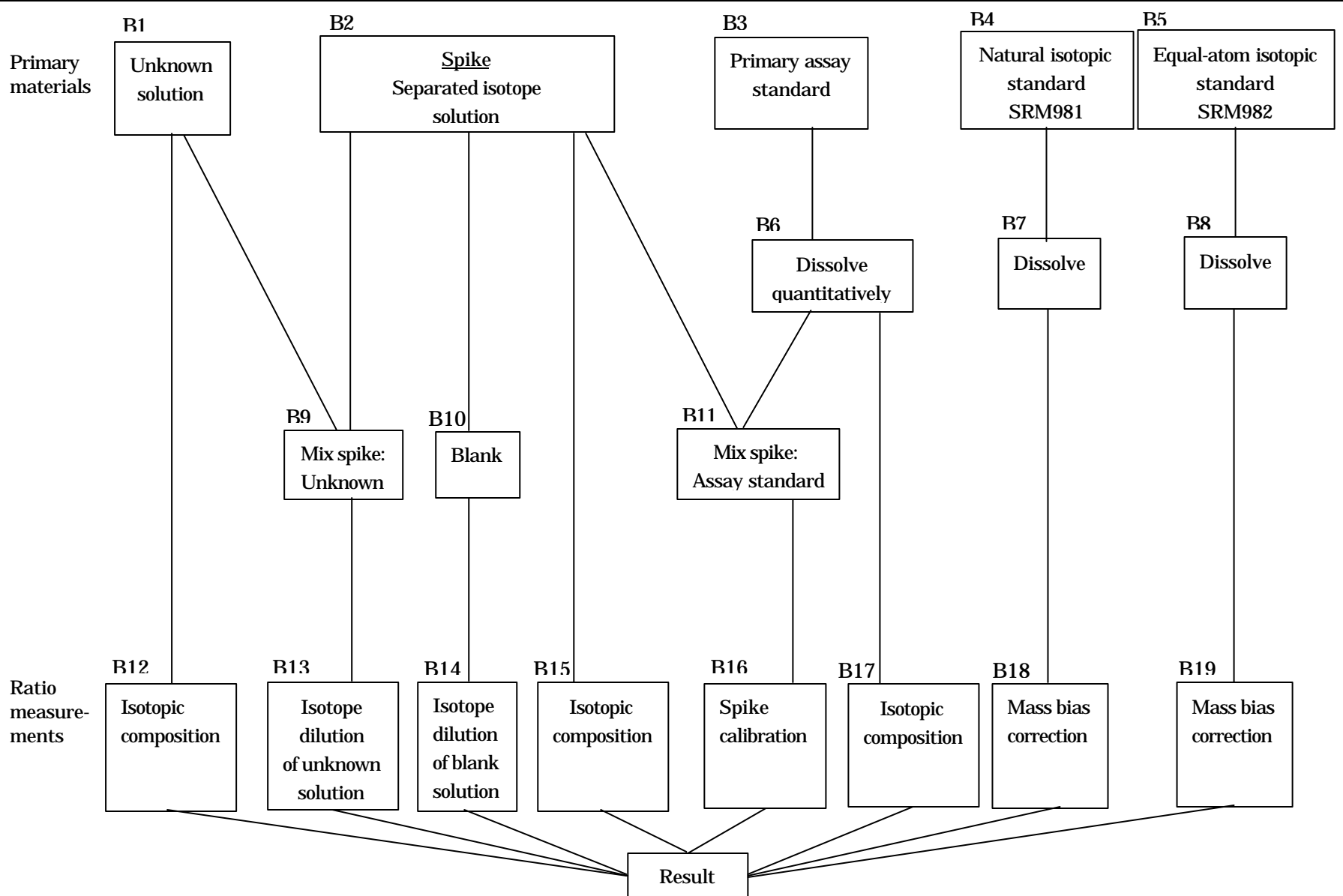


Figure 1. The IDMS process.

which a modified, simpler protocol can be used. In addition, isotopic standards are necessary to calibrate the response of the mass spectrometer. The materials provided for this experiment are listed in Table 1 and are described below.

Table 1. Primary materials provided

Material	Fig. 1 box No.	Form	Isotopic composition	Comment
Unknown sample	B1	Solution	"natural"	Concentration to be determined
Isotopic spike	B2	Solution	206 highly enriched	Used for isotope dilution
Assay standard	B3	Solid	"natural"	High purity metal
Isotopic standards: SRM 981	B4	Solid	"natural"	Good isotopic match for "natural" samples
SRM982	B5	Solid	206 enriched	Good isotopic match for spiked samples

The five materials provided correspond to the materials in the boxes in the top row of Figure 1. From these primary materials, some of which are Standards Reference Materials (SRMs), secondary solutions are prepared of the assay and isotopic, and these are used to prepare the isotope dilution mixes. The secondary materials to be prepared are listed in Table 2 and the detailed procedures are also described below.

Table 2. Secondary materials to be prepared.

Material	Fig. 1 box No.	Procedure	Purpose
Assay standard solutions	B6	Quantitative dissolution	Calibrate spike
Isotopic standard solutions	B7, B8	Dissolution	Determine MS mass bias
Isotopic dilution mixes: Spike: Unknown sample	B9	Mix by Mass	Concentration of unknown
Spike: Reagents	B10	Mix by Mass	Chemical blank
Spike: Assay standard	B11	Mix by Mass	Concentration of spike

#### 4. Primary materials

##### 4.1 Unknown sample (B1)

The sample provided consists of a solution quantitatively prepared from a Pb primary standard of known

isotopic composition. Since lead is one of the few elements whose isotopic composition varies in nature, its isotopic composition needs to be determined. For this experiment, each laboratory will need to measure the isotopic composition of Pb in the sample solution.

Weigh the sample bottle immediately upon receipt, in the heat-sealed plastic bag to obtain a tare mass. Comparing the mass as-received to the mass just prior to analysis will be sufficient to detect any gross changes (although improbable) in the solution between receipt and analysis. The nominal concentration will be provided to obviate the need for a preliminary analysis.

#### 4.2 $^{206}\text{Pb}$ spike solution (B2)

The spike solution has a nominal concentration of approximately  $15 \mu\text{g/g}$  ( $0.075 \mu\text{mol/g}$ ) and the fractional isotopic composition as provided by the vendor, A<sub>1</sub>(206,B2) see Section 8.2, is:

Isotope of lead	A <sub>1</sub> (206,B2)
204	0.000 44
206	0.996 9
207	0.001 98
208	0.000 64

It is difficult to determine experimentally the isotopic composition of the spike with high accuracy since the 206/208 ratio is very large. However, one should make the measurement (B15) to confirm the identity and integrity of the spike, but then use the vendor values in the calculations. As long as the same isotopic values are used for the spike calibration and sample concentration calculations, small errors in the absolute isotopic composition of the spike tend to cancel.

#### 4.3 Isotopic standards

SRM 981, Common Lead Isotopic Standard (B4), has certified isotopic abundances and is near the composition of most natural lead. SRM 981 is a high purity lead metal of 99.9+% purity that has been extruded into wire. This standard is used to determine the mass spectrometer's mass bias and to convert measured isotopic abundances to absolute isotopic abundances for the lead in the unknown sample (B1) and the primary assay material (B3).

SRM 982, Equal-Atom Lead Isotopic Standard (B5), has a certified 208/206 ratio of about 1.0, compared with the 208/206 ratio of 2,1681 for SRM 981. The equal-atom standard is a better isotopic match to the isotope dilution mixes and is better suited for determining their mass bias correction factors.

For each isotopic standard, a piece of wire weighing approximately 100 mg should be dissolved directly in a tared flask using 10 mL of 3 molar  $\text{HNO}_3$  in water and heated on a hot plate (a few drops of high purity  $\text{H}_2\text{O}_2$  can be used to facilitate the dissolution). The

acid concentration is adjusted to 0.5 mol/L  $\text{HNO}_3$  and the final concentration of Pb in solution to  $400 \mu\text{g/g}$  to  $500 \mu\text{g/g}$ . This concentration should be further diluted for ICP-MS measurement so that the major peak,  $^{208}\text{Pb}$ , gives 300 000 counts per second (for the NIST instrument, this concentration is 9 ng/g for  $^{208}\text{Pb}$ ). Dilute nitric acid has the lowest instrument background of the commonly used solvents for ICP-MS, although in general the solvent used should be evaluated for background, washout, and memory for any given element. For Pb, 0.3 mol/L  $\text{HNO}_3$  is an appropriate solvent.

#### 4.4 Assay standard (B3)

A primary assay standard is provided in the form of lead metal having high chemical purity (99,999+%) and nominal natural isotopic composition. This material will be used to calibrate the spike by "reverse isotope dilution". The most accurate results are achieved in isotope dilution analysis when the spike is calibrated, and the unknown samples are analyzed at the same time.

Prepare two standard solutions from two different pieces of metal, each weighing 250 mg to 500 mg. The surface of each metal piece is cleaned using alcohol, water and an acid wash. The surface should be shiny after this cleaning. Extensive acid etching that causes pitting and dulling of the surface should be avoided, since a large surface is more susceptible to oxidation and the resulting potential for negative bias in the assay. Each metal piece is weighed to approximately  $\pm 10 \mu\text{g}$ , or 0.004% for a 250 mg sample. In general, a buoyancy correction should be applied but, for lead, the correction is probably insignificant.

The weighed pieces are placed in tared 250 mL quartz or Pyrex flasks, and are dissolved in the manner described in Section 4.3 for the isotopic standards. When the Pb is completely dissolved, the solutions can be quantitatively diluted to a Pb concentration of about 1 mg/g in 0.5 mol/L  $\text{HNO}_3$ . A balance with 0.1 mg resolution is adequate for this purpose, and the Pb concentration in the resulting solution will have a standard uncertainty of less than 0.001% when prepared as described. The concentrations of these solutions must be accurately known and maintained until used. The molar concentrations should be calculated, as shown in Section 8, using the experimentally determined relative atomic mass.

### 5. Preparation of the isotope dilution mixes

All chemical analysis procedures are limited by the precision of the analytical instrumentation employed. For mass spectrometry, this is the precision of the ratio measurement, and for ICP-MS determination of lead, the ratio measurement relative standard deviation can be controlled to 0.2%, or better. It follows that all sample preparation procedures must be more precise than the

experimental ratio measurement in order to achieve the limiting precision for the whole analysis. Volumetric procedures that approach these levels of accuracy are difficult to implement. Gravimetric procedures\*\* for solution sampling are inherently more precise and accurate and, therefore, are called for in this protocol.

The best IDMS measurements require an optimum mixture of the spike and sample. The uncertainty magnification factor (the propagation of uncertainty in ratio measurement to the uncertainty in concentration) is readily calculated and becomes large as the isotope ratio in the spiked sample approaches either the isotope ratio of the spike ("overspiking") or the isotope ratio of the unknown ("underspiking"). The effect of the uncertainty magnification factor (commonly called "error magnification factor") is dependent on the mass spectrometric precision and the relative enrichments of the spike and natural isotopes. From an uncertainty propagation standpoint alone, the "best" situation occurs when the isotope ratio of the mixture equals the square root of the product of the isotope ratios of the spike and the natural isotope. In practice, other factors must be considered. For example, the best mass spectrometric precision is achieved for ratios near one. Ion counting uncertainty, background corrections, and the relatively limited dynamic range of the ICP-MS with respect to ratio measurement must also be considered. A reasonable rule of thumb is to mix the spike and sample on an equimolar basis.

Equimolar mixing of the spike and sample will result in an isotope ratio of between 1/4 and 4/1 for most elements, assuming that the a spike is a highly enriched isotope (>90% enriched) and the major natural isotope is at least 50%. For lead, this 1:1 rule of thumb is adequate, resulting in a measured isotope ratio  $R(206)$  of about 2,5 ( $R(208)=0,4$ ) (see Section 8).

### 5.1 Spike: unknown sample mixes (B9)

Weigh the unknown solution bottle in the heat-sealed plastic bag and confirm the original mass. Remove the bottle from the plastic bag and remove the heat shrink seal. From this point, precautions should be taken to protect the solution from evaporative loss to maintain its concentration. It is preferable that all samples be taken immediately after opening the bottle. The remaining solution after sampling should be stored in a way

that minimizes evaporative loss. The bottle should be double- or triple-bagged with a small amount of water added between the two outer bags. This procedure is especially important if the bottle is to be stored over a period of months. We have observed transpiration loss from unbagged bottles resulting in analyte concentration increases of up to 0,1% relative over a period of six months.

The unknown solution bottle should be shaken vigorously before the samples are withdrawn. After opening the bottle, carefully wipe the lip and inside lid with a lint-free cloth. These drops would evaporate more rapidly than the bulk solution and degrade the sample. Withdraw the solution samples using a plastic syringe and needle (both 5 mL and 10 mL syringes are convenient). The needle can be inserted through a plastic stopper (or a piece of parafilm) which fits over the top of the unknown solution bottle to avoid evaporative loss while withdrawing the sample.

Remove both the syringe and needle from the unknown solution bottle, and draw the solution in the needle into the syringe. Place the cap back on the bottle to maintain its integrity. Remove the needle on the syringe tip while maintaining upward pressure on the plunger. With the tip up on the syringe, expel any air from the body of the syringe while making sure that there is no solution in the tip. Seal the tip of the syringe with a plastic cap. Although this system is not completely air-tight, evaporative loss is minimal. Nonetheless, weighing should proceed immediately.

Prepare four spike: unknown sample mixes as follows. Weigh each sample into a suitable container in rapid sequence, wiping down the syringe with a damp cloth between weighings to minimize static charge. (Commercial anti-static devices are available.) "Griffin-style" Teflon beakers are convenient sample containers. Deliver the sample dropwise (each drop is about 0,05g). When an appropriate amount of sample has been dispensed, apply an upward pressure on the plunger to pull the remaining solution from the tip into the body of the syringe and then replace the cap. Wipe down the syringe with the damp cloth and reweigh. The delivered sample mass is calculated by difference. A 1g sample can easily be weighed, with accuracies of 20  $\mu$ g to 50  $\mu$ g on a balance with 0,01 mg resolution. or 0.002% to 0.005%. Reproducing the procedure exactly and rapidly gives the best accuracy. since constant biases tend to cancel.

The spike is added to each sample aliquot from the master spike solution (B2). The spike solution provided has a concentration similar to that of the unknown solution, so they should be mixed approximately 1:1. The spike solution added to each sample aliquot is carefully weighed using the procedure described above. A separate syringe and needle are reserved for the spike, to protect its isotopic integrity and to prevent cross contamination among different isotopic materials.

\*\*It is important to note that weighed aliquots of spikes and samples should be mixed directly before any dilutions are performed. Some initial amount of dilution may be necessary in the preparation of the natural assay standard (B3). Such dilutions should be performed gravimetrically and acidified. Ultimately, the concentration levels of the spiked sample must be reduced substantially to stay within the linear dynamic range of the ICP-MS and to avoid dead-time corrections. Once the mixes B9 and B11 are performed and processed, such large dilutions can be made even without the use of calibrated volumetric glassware.

### 5.2 Spike: assay standard mixes (B11)

At the same time as the spike: unknown sample mixes (B9) are prepared, weigh out four 1g aliquots of the spike solution (B2) into clean beakers so that its concentration can be determined in the "spike calibration". Weigh out two of these aliquots before the unknown samples are spiked and two after all unknown samples have been spiked. By this process the integrity of the spike is verified throughout the entire spiking procedure. The spike calibration is done by a "reverse isotope dilution" experiment against the two natural Pb solutions prepared from the assay standard.

The two Pb assay standard solutions that were prepared (Assay1 and Assay2 in B3) have accurately known concentrations of nominally 1 mg/g to 10,mg/g. However, only about 15  $\mu$ g is required for optimal mixing with the spike. A 15 mg aliquot is too small to weigh to the requisite accuracy, so a quantitative dilution must be made from each of the two assay standard solutions. A sixty to six hundred-fold quantitative dilution will give the desired 15  $\mu$ g/g concentration for Pb. A separate, clean syringe and needle are used to weigh out both aliquots from each diluted, primary assay solution.

The four spike: assay standard mixes to be prepared are designated SpikeCal<sub>1</sub>, SpikeCal<sub>2</sub>, SpikeCal<sub>3</sub>, and SpikeCal<sub>4</sub>. The spike solutions in SpikeCal<sub>1</sub> and SpikeCal<sub>2</sub> are weighed out before the unknown samples are spiked, and SpikeCal<sub>3</sub> and SpikeCal<sub>4</sub> are weighed out afterwards. The mixes are prepared by 1:1 mixing of the spike solution and the (diluted) assay standard solution. Calling the two assay solutions Assay<sub>1</sub> and Assay<sub>2</sub>, the mixes should be prepared by adding Assay<sub>1</sub> to SpikeCal<sub>1</sub> and SpikeCal<sub>4</sub>, and adding Assay<sub>2</sub> to SpikeCal<sub>2</sub> and SpikeCal<sub>3</sub>. The experimental design is such that these resulting spike calibration samples will have nearly the same isotopic ratio,  $R(208)$ , as the unknown sample mixes, about 0.4.

### 5.3 Blanks

Analytical blanks are prepared to assess the contamination that occurs in the chemical and instrumental processing. Blank solutions are provided which contain the same purified water and acids that were used to prepare the unknown solutions. Aliquots of these solutions are spiked and processed in a manner similar to that used for the unknown samples. If the magnitude of a "typical" blank for an element and procedure is unknown, it is usual to add 100 times less spike (i.e. 1/100 of the normal spike) to the "blank" solution than is added to the analytical samples. If the blank is 1% of the sample, then it will have the same measured ratio as the samples, and this ratio will be measured with good precision. If the blank is smaller, much larger ratios will be measured, with poorer precision, but the correction is smaller. In some cases, the blank is so small that imprecision in the very large  $R(206)$  ratio results in

an apparent negative blank value. This indicates that the blank is insignificant, which should be the case in this experiment.

Prepare a 10-fold quantitative dilution (by mass) of the master spike (B2) and weigh duplicate 0.1 g aliquots into clean beakers.

## 6. Chemical processing of samples

Isotope dilution requires complete isotope mixing and equilibration, and the sample mixes must be diluted to optimal concentrations for presentation to the ICP-MS. Since all the Pb is in solution and has the same chemical form, the samples are simply treated with high purity acids and heated to ensure this process. All spike: unknown sample mixes, spike: assay standard mixes, and blanks are treated in a similar way.

Rinse down the walls of each beaker with 5 mL of HNO<sub>3</sub>. Cover each beaker with a watch-glass style Teflon lid and heat on a hot plate for several hours. Separate hot plates should be used for each sample type to prevent any chance of cross contamination. For most applications of this method, the covers are then removed and the solutions are taken to dryness. This step is probably unnecessary for the samples and spikes provided for this comparison.

Each sample is diluted to achieve a count rate of about 300 000 counts per second for the major isotope. Although these dilutions are carefully made so that instrumental count rates are similar and restricted to the given range, as mentioned previously, they need not be quantitative since all analytical data are based on the measured isotope ratios. About 20 g of each sample solution is prepared for instrumental analysis. This amount is enough for 4 runs (10  $\times$  1 min) at a flow rate of 0.4 mL/min. In addition, about 200 g of one of the spike calibration samples, for example, SpikeCal<sub>3</sub>, is prepared. This sample is run repeatedly to normalize any drift in instrumental mass bias.

Table 3 lists all the samples that will be prepared for MS ratio measurement. The list shows the number of samples of each type, the ratios to be measured, and identifies the isotopic standard that will be used for the mass bias correction factors for each MS ratio measurement.

## 7. Mass spectrometric measurement

### 7.1 Accurate measurement of ratios by ICP-MS

#### 7.1.1 Deadtime correction

Electron multiplier detectors used in the ion counting mode, the most common detection practice in ICP-MS, must be calibrated for deadtime, the interval following registration of an ion during which a second ion will not be detected. The Nd 144/145 ratio (approximately 3:1) is measured over a range of count rates using

Table 3. Summary of ratio measurements.

Fig 1 box No.	Material	<i>m</i>	Isotope Ratio(s) Measured	Calculations	Comment	SRM for mass bias correction
B12	Unknown	1	All isotopes, relative to 206	§ 8.2	Isotopic composition	981
B13	Spike: unknown mix	4	208/206	§ 8.7	Concentration of unknown by ID	982 through SpikeCal <sub>3</sub>
B14	Spike: reagents mix	2	208/206	§ 8.6	Procedural blank	982 through SpikeCal <sub>3</sub>
B15	Spike	1	All isotopes, relative to 206	§ 8.2	Compare with vendor composition	Check with 982
B16	Spike: assay standard mix	4	208/206	§ 8.5	Spike calibration ID	982
B17	Assay standard	1	All isotopes, relative to 206	§ 8.2	Isotopic composition	981
B18	"Natural" isotopic standard SRM 981	1	208/206	§ 8.1	Determine F	-
B19	Equal-atom isotopic standard SRM 982	1	208/206	§ 8.1	Determine F	-

*m* = number of solutions or mixes to be prepared and measured on the MS instrument

a series of carefully prepared Nd standards at fixed concentration levels to determine the magnitude of the deadtime and to assess the linearity of corrected data. The deadtime should be an adjustable parameter in the ICP-MS instrument's controlling software. Count rates should be limited to minimize the uncertainty in this correction.

#### 7.1.2 Limiting signal levels

A second problem with electron multiplier detectors is the loss in gain at high count rates. Although the use of ion counting reduces the effect of this sag in gain on ratio measurement, ion counts will be lost due to changes in efficiency of the detector, and the larger the signal the greater will be the loss. This leads to non-linearity in ratio measurements and, in contrast to deadtime non-linearity, it is inherent that the effect is not correctable. Thus, the signal levels should be limited to 250 000 to 300 000 counts per second, or less for the most accurate measurements.

#### 7.1.3 Ratio measurement

It is recommended that all analytical data be taken in the peak-jump mode of operation. The mass scale is adjusted to be centered on the peak tops of the analyte isotopes, and is tested using multiple points per peak. Experience with one type of ICP-MS instrument indicates that when correctly centered, there should be less than 1% decrease in signal intensity per 0.02 mass units on either side of the peak top. Isotope ratio data is collected using one point per peak with 10 ms dwell times when measuring peaks of equal intensity. For lead spiked samples, use of 10 ms and

20 ms dwelltimes for masses 206 and 208, respectively, will modestly improve the precision by improving the counting statistics.

#### 7.1.4 Mass bias corrections

All mass spectrometers exhibit mass bias which results in a measured isotopic ratio that is systematically different from the true isotopic ratio for an element in a sample. The mass bias is normally greatest at low mass and smallest at high mass. For ICP-MS this bias changes with instrumental operating conditions and drifts with time. The drift can be significant relative to the precision of ratio measurements. Thus, to obtain both the highest precision and accuracy it is necessary to measure and correct for the mass bias and its drift during instrument operation.

The isotopic composition of Pb varies significantly in nature. Thus, isotopic reference materials are required (and are available) for mass bias measurement. A practical approach is to use a synthetic mix of natural and spike isotopes (i.e. SpikeCal<sub>3</sub>) as a working isotopic control with approximately the same ratio as samples for the measurement of drift. The isotopic ratio of this control is determined by comparison with the isotopic standard SRM 982 for lead. Drift corrections are made by linear interpolation between the times when SpikeCal<sub>3</sub> is run.

#### 7.1.5 Interferences

Interference is a potential source of error for ICP-MS, and has been the subject of much discussion. For IDMS, the ability to measure natural isotopic ratios from unspiked samples implies interference-free

measurement. For Pb, interference is generally not a problem, with the exception that  $^{204}\text{Pb}$  is subject to interference by  $^{204}\text{Hg}$ . This interference can be determined and corrected by measurement of the  $^{202}\text{Hg}$  in the determination of the isotopic composition of the Pb in the assay standard and sample. Hg may be present in either the laboratory environment or in the reagents. The correction should be small and interference should not be a significant source of uncertainty in this case.

## 7.2 Data collection protocol

Figure 1 identifies the eight types of ratio measurement required for the complete experiment. These are characterized by the "natural" isotopic composition measurements of the unknown (B12) and the assay standard (B17); the isotopic composition of the spike (B15); the mass bias correction measurements from the "natural" isotopic standard, SRM 981 (B18), and the equal-atom standard, SRM 982 (B19); and the ratio measurements of the isotope dilution mixes (B13, B14, and B16). It is best to measure ratios of approximately the same intensity together. It is especially important to make sure that a thorough washout is done both before and after measurement of the 206 spike. These measurements are summarized in Table 3 and the calculations associated with them are given below in Section 8.

For the isotope dilution mixes the order of sample measurement is: 0.3 mol/L nitric acid, SRM 982, SpikeCal<sub>3</sub> (working isotopic control). The samples, blanks, and spike calibrations are then run in random order with the working isotopic control bracketing every two samples. A set of 10, one-minute ratio measurements is carried out for each sample. Each sample is typically introduced into the instrument for 2 minutes before the data is collected.

There is no inherent reason that the ratio  $R(207)$  should not be used instead of, or in conjunction with,  $R(208)$ , if a complete set of ratios is measured for this isotope pair as well. One of the advantages of IDMS with elements having three or more isotopes is that internal consistency can be checked by using all of the available isotopic information. However, a larger and more uncertain drift correction may result if the measurement time per sample is increased. The calculation equations given in Section 8 apply when using the  $R(208)$  ratio (or its reciprocal).

## 8. Calculation equations

The calculations that will be applied to the data are described in the following subsections.

### 8.1 Mass bias correction factor and normalization of ratios

For measured 208/206 ratios, the correction factor for isotopic discrimination is determined by:

$$F(208) = \frac{R_c(208)}{R_m(208)} \quad (1)$$

where  $F(208)$  is the mass bias correction factor for 208/206 ratios,  $R_c(208)$  is the certified 208/206 isotopic ratio, and  $R_m(208)$  is the measured 208/206 ratio for the certified material. Measured 208/206 ratios should be normalized to an appropriate isotopic standard following

$$R_n(208) = F(208) \cdot R_m(208). \quad (2)$$

Note that the subscripts m, c, and n are used to signify *measured*, *certified*, and *normalized* ratios, respectively.

Ratios of the other isotopes should be measured and normalized in a similar manner. Thus,  $R_m(204)$  and  $R_m(207)$  refer to measured 204/206 (corrected for  $^{204}\text{Hg}$ ) and 207/206 isotope ratios, respectively, and  $R_n(204)$  and  $R_n(207)$  refer to the corresponding normalized ratios.

Note that two complete sets of mass bias correction factors are obtained: one set based on measurements of SRM 981 and the other on SRM 982. As indicated in Table 3, the mass bias correction factors based on SRM 981 should be used for the samples corresponding to boxes B12 and B17 of Figure 1, and the correction factors based on SRM 982 should be used for the samples corresponding to boxes B13, B14, B15 and B16.

### 8.2 Determination of isotopic abundances

Relative isotopic abundances, expressed in terms of atom fractions,  $A_f()$ , are calculated as follows:

$$A_f(208) = \frac{R_n(208)}{1 + R_n(208) + R_n(207) + R_n(204)} \quad (3)$$

$$A_f(207) = \frac{R_n(207)}{1 + R_n(208) + R_n(207) + R_n(204)} \quad (4)$$

$$A_f(206) = \frac{1}{1 + R_n(208) + R_n(207) + R_n(204)} \quad (5)$$

$$A_f(204) = \frac{R_n(204)}{1 + R_n(208) + R_n(207) + R_n(204)} \quad (6)$$

### 8.3 Determination of relative atomic masses

Relative atomic masses are given by:

$$\begin{aligned} A_r = & 207.976\ 641 \times A_f(208) \\ & + 206.975\ 885 \times A_f(207) \\ & + 205.974\ 455 \times A_f(206) \\ & + 203.973\ 037 \times A_f(204). \end{aligned} \quad (7)$$

#### 8.4 Determination of the concentration of the assay standard solutions

The concentrations of the (two) assay standard solutions, Assay<sub>1</sub> and Assay<sub>2</sub> are calculated from:

$$C_{B6} = \frac{(M_{B3}/A_r(B3))}{M_{sol}}, \quad (8)$$

where  $M_{B3}$  is the mass of the primary assay standard lead (box B3 of Figure 1) multiplied by the dilution factor ( $\approx 0,03$ ) mentioned in Section 5.2,  $M_{sol}$  is the mass of the resulting solution, and  $A_r(B3)$  is the calculated relative atomic mass for the assay standard lead, based on the MS measurements corresponding to box B17 of Figure 1. The quantity  $C_{B6}$  is usually expressed in moles of total lead per gram of solution.

#### 8.5 Determination of the concentration of the spike solution

The Pb concentration of the spike solution, box B2 of Figure 1, is calculated from the results of the "reverse isotope dilution" as follows.

$$C_{B2} = \frac{M_{B6} \cdot C_{B6}}{M_{B2}} \times \left( \frac{A_r(208,B17) - R_n(208,B16) \times A_r(206,B17)}{R_n(208,B16) \times A_r(206,B6) - A_r(208,B2)} \right), \quad (9)$$

where  $C_{B2}$  is the concentration of total lead (usually expressed in mol/g) in the spike solution;  $M_{B2}$  and  $M_{B6}$  are the masses of spike solution (B2) and assay standard solution (B6), respectively, that were mixed together to create the spike: assay standard mix (i.e. the "spike calibration" sample, (B11) of Figure 1); and  $C_{B6}$  is the concentration of Pb in the assay standard solution (B6). The isotope ratio in (9), denoted  $R_n(208,B16)$ , is the (normalized)  $R(208)$  ratio for the spike calibration mix, and corresponds to (B16) of Figure 1. Two sets of atom fractions are used in (9).  $A_r(206,B17)$  and  $A_r(208,B17)$  denote the calculated 206 and 208 atom fractions for the assay standard lead, as obtained from the isotope ratio measurements corresponding to (B17) of Figure 1. On the other hand,  $A_r(206,B2)$  and  $A_r(208,B2)$  denote the atom fractions the spike solution as supplied by the vendor, rather than the measured values obtained by the ratio measurements corresponding to (B15) of Figure 1. Although the measured fractions are subject to instrument bias and the vendor-supplied fractions can be of variable metrological quality, the effects of these bias sources cancel in the final calculation of the unknown sample concentration. We have observed that spike calibrations can vary by over 2 % relative, while the corresponding data for the concentration of an unknown varies by only 0,5 % relative.

#### 8.6 Determination of the amount of the blank

The amount of the blank correction,  $Z$ , usually expressed in mol/g, is calculated as follows.

$$Z = \frac{M_{B2} \times C_{B2}}{M_{B1}} \times \left( \frac{R_n(208,B14) \times A_r(206,B2) - A_r(208,B2)}{A_r(208,nat) - R_n(208,B14) \times A_r(206,nat)} \right), \quad (10)$$

where  $M_{B1}$  = aliquot mass of the blank solution provided,  $M_{B2}$  = mass of spike (B2) used in preparing the blank (B10), multiplied by the dilution factor ( $\approx 0,1$ ) mentioned in section 5.3,  $A_r(206,B2)$  and  $A_r(208,B2)$  are the (vendor-supplied) atom fractions for the spike, and  $A_r(208,nat)$  and  $A_r(206,nat)$  are the atom fractions of the "natural" lead in the blank. For the purposes of this experiment, it will suffice to use  $A_r(208,nat) = 0,512$  and  $A_r(206,nat) = 0,268$ . The calculated concentration of the unknown solution should not be sensitive to these values.

#### 8.7 Determination of the concentration of the unknown solution

The concentration of the unknown solution, uncorrected for blank, is determined as follows:

$$C_{B1} = \frac{M_{B2} \times C_{B2}}{M_{B1}} \times \left( \frac{R_n(208,B13) \times A_r(206,B2) - A_r(208,B2)}{A_r(208,B12) - R_n(208,B13) \times A_r(206,B12)} \right), \quad (11)$$

where  $M_{B1}$  and  $M_{B2}$  are the masses of the unknown solution (B1) and spike solution (B2), respectively, that were mixed to produce the sample corresponding to box B8 of Figure 1. In addition,  $C_{B2}$  is the calculated concentration of the spike solution, from (9);  $R_n(208,B13)$  is the normalized  $R(208)$  ratio obtained for the spike: unknown mix (corresponding to box B13);  $A_r(206,B12)$  and  $A_r(208,B12)$  are the calculated atom fractions for the "natural" lead in the unknown sample, obtained from the isotope ratio measurements indicated in box B12 of Figure 1; and  $A_r(206,B2)$  and  $A_r(208,B2)$  are again, the vendor-supplied atom fractions for the spike.

The value of  $C_{B1}$  from (11) is expressed in moles per gram. To convert this concentration to units of grams of lead per gram of solution, multiply by the relative atomic mass of lead in the unknown. Thus, if we denote by  $C_{B1} \cdot$  the concentration after conversion to units of grams per gram,

$$C_{B1} \cdot = C_{B1} \times A_r(B1), \quad (12)$$

where  $A_r(B1)$  is the calculated relative atomic mass of lead in the unknown, based on the isotope ratio measurements corresponding to box B12 of Figure 1.

A convenient way to implement these related calculations is by a suitably designed computer spreadsheet.

### 9. Estimation of uncertainties

The purity of the primary assay standard (B3) needs to be established by as complete a determination of impurity elements as possible. This effort also must include an analysis for dissolved oxygen, hydrogen and nitrogen gases. Individual impurity elements and gases found in the B3 material will each have an uncertainty (usually Type A[2]) from their determination. Elements not found will nonetheless have an upper limit defined by the detection capabilities of the method(s) used for the analysis. A conservative approach is to assume that a non-detected impurity is present at a level midway between zero and this upper limit. The corresponding uncertainty would then be plus or minus this midpoint value.

The spike calibration steps have uncertainties associated with weighing, normalization of ratios, including the isotopic standards uncertainties, and ratio measurement. The same components enter into the estimation of uncertainties in the sample measurement steps, with the addition of sample material heterogeneity when the method is applied to real samples.

As pointed out in Section 8.5, uncertainties in the atom fractions of the spike would appear to add an uncertainty to the overall measurement process. However, since these atom fractions are used in both the spike calibrations and sample measurement, these factors will cancel as a first approximation. For most elements this same argument can be made for the uncertainties in the natural atom fractions. However, lead's natural variability results in potential real differences in the natural isotopic abundances between the assay material and the sample.

### 10. Study III

The protocol detailed here was provided to ten CCQM metrology laboratories for their use in Study III, the determination of lead in water. The unknown sample and calibration materials described in the protocol were prepared at the NIST and provided to all study participants, along with a set of spreadsheets containing example calculations from the NIST lead data from Study I. Study III was designed so that sample and spike material handling should not result in any significant blank correction when compared to the analyte level in the sample. However, the participants were advised that dilutions should be made shortly before ratio measurements are to be made, and that clean environments and ultra-pure acids and water should be used.

The analysis kits contained the following items:

- 1) One sample solution bottle
- 2) One blank solution bottle
- 3) One spike solution bottle
- 4) One vial of SRM 981 and a certificate
- 5) One vial of SRM 982 and a certificate
- 6) The spike material supplier's data
- 7) A syringe typical of the kind used at the NIST to weigh solutions as described in the protocol
- 8) A copy of the protocol with cover letter.

Results from Study III were presented at the CCQM meeting at the BIPM in February, 1997.

### References

1. BIPM Comité Consultatif pour la Quantité de Matière, 1996. 2, 38 p.
2. Guide to the *Expression of Uncertainty in Measurement*, ISBN 92-67-10188-9, 1st Ed., Geneva, Switzerland, ISO, 1993.